Effect of Acetylation on Sorption of Water by Cellulose

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IN a recent paper [2] the authors of this report analyzed the contribution of the free amino group to the water-sorbing properties of casein. A series of samples with different amounts of N-benzoyl substitution was prepared, and absorption isotherms were determined. The contribution of the amino group at the various humidities studied was found by graphical analysis to be directly proportional to the amount unsubstituted. The data were calculated on a total nitrogen basis, thus correcting for the amount of benzoyl radical introduced. The original assumption—that the N-benzoyl group does not absorb water—was verified by the results. One-fourth of the water sorbed by casein was thus attributed to the free amino group.

The possibility of an analogous treatment of data on the cellulose-cellulose acetate system occurred to us. Sheppard and Newsome [3, 4] studied this system and concluded that, in agreement with the generally accepted idea, esterification greatly decreases the water-sorbing power of the hydroxyl group. The discussion by Valko in *Cellulose and Cellulose Derivatives* [7, page 385] follows this treatment and reproduces figure 7 of reference 3. Smith and Childs, in *Matthews' Textile Fibers* [5], give a similar discussion.

Through the courtesy of S. E. Sheppard and J. Russell, adsorption isotherms obtained by P. T. Newsome upon cellulose samples of 0, 4.2, 37.6, 39.2, 40.5, 43.5, and 45.0 percent acetyl groups were made available to us. Calculation of the isothems in terms of the amount of cellulose residue present (that is, correcting for the dilution due to substitution with acetyl) shows that for these data the water uptake is not diminished by acetylation. The control samples and the most highly acetylated (cellulose triacetate contains 44.8 percent acetyl) ones show little difference in water absorption. There is a distinctly higher absorption of water in the 37.6, 39.2, and 40.5 percent acetyl samples in the region 50 to 100 percent relative humidity. Sorption values at a series of relative humidities, taken from the smoothed curves of the data, are given in Table I. Illustrative isotherms for cellulose, 39.2 percent acetyl cellulose, and completely acetylated (45.0 percent) cellulose, calculated on both a cellulose-content basis and a weight basis, are shown in Figure 1.

The data of Figure 1 and those presented later cannot be expected to reflect only the effect of esterification of hydroxyl groups. It is well known that the initial cellulose sample, conditions of acetylation, and subsequent history of the sample all have some effect on its moisture absorption. Moreover, acetylation appears to have a secondary effect of producing a more open or porous structure in the intermediate degrees of acetylation, accounting for the higher sorption at relatively high humidities of the 39.2 percent acetyl sample. The completely acetylated sample, on the same basis, does not have so porous a structure and approaches the water uptake of the initial cellulose more closely.

Sheppard and Newsome [3, figure 7; 7, page 385] also plotted the integrated water absorption, 0–100 percent relative humidity, against acetyl content for a group of normal cellulose and mercerized cellulose samples. In Table II, these data are recalculated on

TABLE I. MOISTURE REGAIN OF CELLULOSE ACETATE, CALCULATED ON THE CELLULOSE CONTENT

Relative humidity (%)	Moisture regain, Percent acetylation 0%	4.2%	37.6%	39.2%	40.5%	43.5%	45.0%
10	1.4	1.3	1.1	1.4	0.9	1.3	0.8
20	2.4	2.2	2.2	2.5	1.8	2.2	1.7
40	4.0	3.6	4.3	4.3	3.7	3.6	3.4
60	5.3	5.3	7.2	6.9	6.8	5.8	5.1
80	7.9	7.8	12.5	11.6	11.2	9.4	7.7
100	17.5	16.5	21.4	21.4	21.6	18.4	15.3

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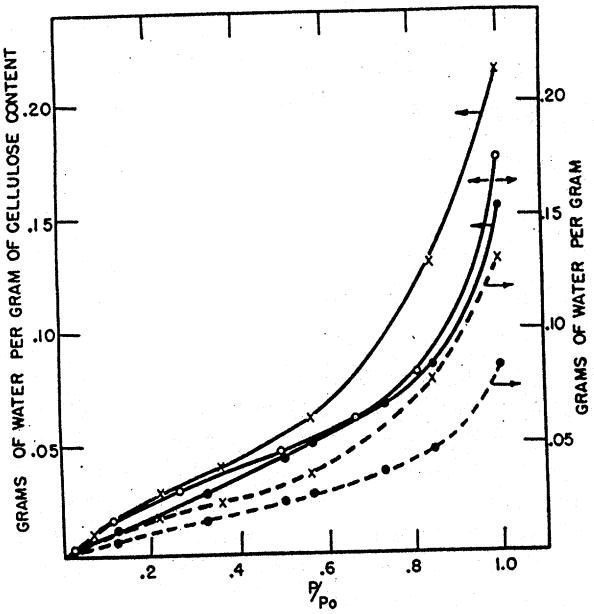

FIG. 1. *Water absorption of cellulose acetate. Circles = Cellulose. Crosses = 39.2 percent acetyl cellulose. Black dots = 45.0 percent acetyl cellulose. Solid lines = Data calculated on a cellulose-content basis. Dotted lines = Data calculated on a weight basis.*

the basis of the cellulose content of the samples. The linear decrease with increasing acetyl content shown by the original calculation is eliminated in the case of the normal cellulose. It is not clear whether the exact agreement of sorption and cellulose content over the whole range of acetylation is fortuitous or is due to the use of "fibrous" acetylation. The mercerized samples have a higher absorption in the intermediate range and on complete acetylation approach the absorption of the completely acetylated "fibrous" material. An exact interpretation of these data in terms of the hygroscopicity of the hydroxyl and acetyl ester group is difficult, for the effect of acetylation upon crystallinity or accessibility of the reactive groups has not been determined. The general conclusion holds, however, that cellulose acetate has essentially the same hygroscopicity as cellulose when calculated upon a molar basis.

Such a conclusion cannot be interpreted as indicating that the hydroxyl group is not an absorbing center, for Sheppard and Newsome [4] have published data on the homologous series of acyl celluloses which show that the propionyl, butyryl, and higher cellulose esters have definitely lower water absorption. The 100-percent relative humidity values from their data, and the recalculation on the basis of the cellulose content of the derivatives, are given in Table III. The only major difference disclosed by considering the data on the basis of cellulose content is in the acetyl derivative, where the effect of acetylation on water absorption is small. The higher esters show pronounced decreases in water absorption, reaching a maximum effect in the caproate and heptoate esters, as Sheppard and Newsome concluded.

Similar calculations have been made on the water absorption of commercial viscose rayon, cuprammonium rayon, and acetate yarn. The differences in chemical treatment in the three processes preclude exact analysis of the data. However, Wiegerink's data, as recalculated by Toner, Bowen, and Whitwell [6], give the adsorption value at 35.6°C and 65 percent relative humidity of viscose rayon as 13.7 percent regain, of cuprammonium as 12.5 percent, and of acetate yarn as 6.5 percent, which, assuming 40 percent acetyl content, is 10.8 percent on a cellulose basis. The commercial standards of 11 percent regain for viscose and 6.5 percent for acetate, although lower than the actual regain, are in almost exact agreement on a cellulose basis.

It is apparent that the original purpose of our investigation—the determination of water absorption

TABLE II. INTEGRATED WATER ABSORPTION * (0–100% R.H.) OF CELLULOSE ACETATE PREPARED FROM NORMAL AND MERCERIZED CELLULOSE, AT 30°C

Acetyl content (%)	Water absorption: Weight basis	Water absorption: Cellulose-content basis
Normal cellulose		
0	330	330
10	300	330
24	250	330
37	200	320
45	175	320
Mercerized cellulose		
0	510	490
0	470	
7	485	520
34	365	550
38	300	485
40	283	470
42	270	465
44	240	430

* Area under the curve of percent regain vs. relative humidity.

TABLE III. SORPTION PROPERTIES OF CELLULOSE TRIESTERS AT 25°C

Ester	No. of carbon atoms	Moisture regain at 100% R.H. Weight basis (%)	Moisture regain at 100% R.H. Cellulose-content basis (%)
(Cellulose)	0	18.8	18.8
Acetate	2	10.0	18.1
Propionate	3	4.4	9.2
Butyrate	4	3.5	8.2
Valerate	5	1.7	4.4
Caproate	6	0.9	2.6
Heptoate	7	0.8	2.5
Caprylate	8	0.9	3.0
Pelargonate	6	1.0	3.7

by the hydroxyl group as a function of relative humidity—cannot be accomplished with the data at hand. Sorption isotherms upon nitrocellulose, cellulose ethers, or higher cellulose esters of known degree of substitution are required for such calculations. We have not found complete isotherms for these series, but published data indicate that the hygroscopicity of these cellulose derivatives is essentially eliminated as complete substitution is approached. Ethylcellulose [1] shows a linear decrease in moisture absorption at 70 percent relative humidity with increasing degree of substitution. The data extrapolate to zero absorption at complete substitution.

Summary

The data of Sheppard and Newsome on water absorption by cellulose esters have been recalculated on the basis of the cellulose content of the samples. The apparent decrease in water absorption of cellulose caused by acetylation is primarily a "dilution" effect. Cellulose acetate has essentially the same hygroscopicity as cellulose when calculated on a molar basis.

Esterfication with propionyl, butyryl, and higher acyl groups definitely decreases the water absorption of cellulose. The maximum diminution, about 85 percent, is obtained by caproate and heptoate substitution.

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